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Method for pickling metallic surfaces by using ~~alkoxylated alkynole~~

The present Application relates to a process for pickling metallic surfaces by treating the metallic surface with a composition which comprises water, at least one acid, an alkyne alkoxylate and optionally further additives. In a preferred embodiment, the alkyne alkoxylate is used together with a complexing agent.

In pickling, the surface of a material is treated with a pickle and thus changed by a chemical method. Here, undesired surface layers are removed and, if appropriate, protective or effect layers are built up. In the case of metallic surfaces, pickling serves in particular for removing various oxide layers, for example rust or scale layers, and/or other impurities, for example greases, oils or lime, from the surface and/or for activating and/or protecting the surface. An example of a protective treatment is an acidic phosphating of an iron or steel surface. Here too, a substantial element is a pickle attack on the metal. In phosphating with an acidic zinc phosphate solution, a large number of H^+ ions are consumed directly at the metal surface through the pickle attack of the acid on the metal, producing a local increase in the pH. Only as a result of this is the solubility product with zinc phosphate exceeded so that zinc phosphate is deposited in a thin layer on the surface.

Aqueous, inorganic or organic acids, in particular hydrochloric acid, phosphoric acid or sulfuric acid, and as a rule assistants, for example surfactants, are used for pickling. Although the acid is intended to attack the surface layers and, if appropriate, also the metal itself, it is as a rule undesirable if excessive amounts of metal are dissolved. On the one hand, a great deal of pickling acid is consumed thereby and the pickle is contaminated with dissolved metal ions. The pickling bath must accordingly frequently be renewed. On the other hand, however, the surface - in particular in the case of iron or nickel - may also be damaged by so-called hydrogen embrittlement. Pickling inhibitors which are intended to prevent or at least greatly slow down the dissolution of the base metal without substantially hindering the dissolution of the surface layers are therefore usually added to formulations for pickling. Pickling with the use of inhibitors is also occasionally referred to as inhibited pickling.

It is known that alkynols, for example 2-butyne-1,4-diol, 1-propyn-3-ol or 1-ethynyl-cyclohexanol, can be used as pickling inhibitors. By way of example, reference may be made to US 3,658,720, US 3,969,260 or JP-A 60-208 487. WO 99/32687 discloses the use of 2-butyne-1,4-diol as an inhibitor in the acidic phosphating of steel strip galvanized on one side.

When handling alkynols, particular caution must be exercised. 2-Butyne-1,4-diol and 1-propyn-3-ol are classified as toxic and carcinogenic, respectively.

Alkyne alkoxylates are in principle known, for example from DE-A 22 41 155. They are used, inter alia, as bright electroplating additives in the electroplating of nickel or cobalt, as disclosed in US 3,804,727, 3,814,674 or US 4,832,802. Alkoxylated alkynols are not classified as toxic or carcinogenic.

US 3,004,925 discloses the use of ethoxylated butynediol derivatives and ethoxylated propynol derivatives as a corrosion inhibitor in aqueous solutions. The OH groups are in each case modified with $-(CH_2-CH_2O)_x$ groups, where x has a value of from 3 to 25. Furthermore, the disclosed alkynols additionally have one or more alkyl, aryl, cycloalkyl and aralkyl groups. Unsubstituted butynediol or propargyl alcohol is not disclosed.

US 5,215,675 discloses compositions for removing finishes from surfaces, which comprise from 10 to 50% of water, from 3 to 15% of a peroxide and from 40 to 70% of ethyl lactate. The composition may furthermore optionally also comprise ethoxylated butynediol as a corrosion inhibitor, and an acid. In a further embodiment, a composition which comprises 55 to 60% of butyrolactone, from 30 to 32% of aqueous hydrogen peroxide, 9.5% of formic acid, 1% of ethoxylated butanediol, 0.5% of Na_4EDTA and 4% of surfactant is disclosed.

It is an object of the present invention to provide a process for pickling metallic surfaces, in which butynediol or propynol are replaced by suitable substitutes, and in which better pickling inhibition is nevertheless achieved. We have found that this object is achieved by a process for pickling metallic surfaces, in which the metallic surface is treated with an acidic aqueous formulation which comprises at least the following components:

(a) from 60 to 99.99% by weight of a mixture of water and at least one acid,

(b) from 0.01 to 2% by weight of at least one alkyne alkoxylate of the formula

$$HC{\equiv}C-CH_2-O(-CH_2-CHR^1-O-)_nH$$

or

$$H(-O-CHR^1-CH_2-)_n-O-CH_2-C{\equiv}C-CH_2-O(-CH_2-CHR^1-O-)_{n'}H,$$

where the radicals R^1 in each case independently of one another are H or methyl and the indices n and n', independently of one another, are from 1 to 10, and

(c) from 0 to 38% by weight of one or more additives and/or assistants.

In a preferred embodiment, the pickling inhibitor is used in combination with a water-soluble complexing agent.

Regarding the invention, the following may be stated specifically:

The novel process can in principle be used for pickling metallic surfaces of various types. The metals may be pure metals as well as alloys. Examples comprise surfaces of iron, cast iron, steel, nickel, zinc, brass or aluminum, and in each case the top metal layer, which is in direct contact with the formulation, is meant. The metallic surface may also be, for example, surface-hardened steel, such as hot-galvanized and zinc-plated steels. The process is particularly suitable for pickling surfaces of (cast) iron, steel or aluminum, very particularly preferably for steel surfaces. The process is particularly suitable for pickling surfaces of strip metals, for example for steel or aluminum.

The metallic surfaces may be outer surfaces of metallic materials, for example the surface of metallic strips, sheets or irregularly shaped workpieces, such as machine parts. However, they may also be inner surfaces, such as the inner surfaces of pipelines, boilers, chemical plants or the like.

In the novel pickling process, undesired surface layers and impurities are removed and, if appropriate, protective and/or effect layers are built up. The term pickling includes the phosphating of metallic surfaces. Undesired surface layers may be in particular inorganic layers, for example substantially oxidic layers, such as rust layers, scale layers or layers which are formed in the rolling of metals, for example of steel. They may also be layers applied for temporary corrosion protection, for example phosphate layers or layers of other materials, for example carbonate layers, such as lime layers or patinas. Undesired layers may furthermore be thin layers of organic materials, for example grease or oil layers.

The formulation used for the novel process comprises, as component (a), water and at least one acid, together in an amount of 60 – 99.99% by weight. The stated percentages here and below are always based on the amount of all components of the formulation.

The total amount of water and acid is preferably from 70 to 99.99%, very particularly preferably from 80 to 99.99, % by weight.

The acid may be an inorganic acid, for example hydrochloric acid, hypochlorous and chlorous acid, sulfuric acid, phosphoric acid or phosphorous acid, or an organic acid, for example formic acid, methanesulfonic acid, acetic acid, citric acid, succinic acid or amidosulfonic acid. Of course, mixtures of different acids may also be used, for example mixtures of hydrochloric acid and phosphoric acid. The acid is preferably hydrochloric acid, sulfuric acid, methanesulfonic acid or phosphoric acid.

The respective amount of water and acid depends on the one hand on the intended use of the formulation and also on the type of acid. Whereas, with the use of phosphoric acid, the solvent can in particular cases consist exclusively of concentrated

(i.e. 85% strength) phosphoric acid, greater dilutions are advantageous with the use of acids other than phosphoric acids. If acids other than phosphoric acid are used, the formulation comprises, as a rule, at least 50, preferably at least 60, % by weight of water. The total amount of water in the formulation is calculated here as the sum of the water which is added together with the acid and that which is added in pure form or in the form of solutions or other materials.

The component (b) in the formulation used for the novel process comprises from 0.01 to 2% by weight of at least one alkyne alkoxylate of the formula

$$HC{\equiv}C\text{-}CH_2\text{-}O(\text{-}CH_2\text{-}CHR^1\text{-}O\text{-})_nH \quad (I)$$

or

$$H(\text{-}O\text{-}CHR^1\text{-}CH_2\text{-})_n\text{-}O\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2\text{-}O(\text{-}CH_2\text{-}CHR^1\text{-}O\text{-})_{n'}H \quad (II).$$

The indices n and n', independently of one another, are from 1 to 10. It is known to a person skilled in the art that such alkoxy groups are obtainable in particular by oxyalkylation or starting from industrial polyglycols. Said values for n are therefore average chain lengths, where the average value need not of course be a natural number but may also be any desired rational number. n and n' are preferably a number from 1 to 3.

The radicals R^1 in (I) and (II) are in each case independently of one another H or methyl. The alkyleneoxy groups may be groups derived exclusively from ethylene oxide units or groups derived exclusively from propylene oxide. However, they may also be groups which have both ethylene oxide units and propylene oxide units.

Polyoxypropylene units are preferred

Of course, mixtures of (I) and (II) and/or mixtures of different compounds (I) or different compounds (II) may also be used. Compound (I) is preferably used.

From 0.05 to 2% by weight of (I) and/or (II) are preferably used, particularly preferably from 0.075 to 1.5, very particularly preferably from 0.1 to 1.0, % by weight. All concentration data are based on the ready-to-use composition. It is of course possible first to prepare concentrate, which is diluted to the desired concentration only on site.

The amount of (I) and/or (II) also depends on the type and amount of the acid used and on the temperature at which the formulation is to be used. The higher the acid concentration, the higher the concentration of pickling inhibitor (I) and/or (II) used in each case should generally also be. The higher the temperature, the higher the

concentration of pickling inhibitor should also generally be. The amounts stated below have proven particularly useful for use at room temperature:

Amount of acid [% by weight]	Pickling inhibitor [% by weight]
5	0.03 - 0.1
10	0.05 - 0.2
15	0.1 - 0.3
20	0.15 - 0.4

The compounds used are obtainable in a known manner by oxyalkylation of butynediol or propargyl alcohol, as described, for example, in DE-A 22 41 155 or US 3,814,674.

The formulation used for the process furthermore comprises, as a rule, one or more additives or assistants, even if the addition thereof is not absolutely essential in every case.

The amount of such additives is from 0 to 38, preferably from 0.01 to 30, particularly preferably from 0.1 to 20, % by weight.

Assistants comprise in particular from 0.01 to 20% by weight of at least one surface-active substance. Preferably from 0.1 to 10, particularly preferably from 0.5 to 8, % by weight of the surface-active substance are used. Examples of suitable surface-active substances comprise conventional anionic, cationic or nonionic surfactants.

Particularly suitable nonionic surfactants are:

- Alkoxylated C_8-C_{22}-alcohols, such as fatty alcohol alkoxylates, oxo alcohol alkoxylates and Guerbet alcohol ethoxylates: the alkoxylation can be effected with ethylene oxide, propylene oxide and/or butylene oxide. Block copolymers or random copolymers may be present. They usually comprise from 2 to 50, preferably from 3 to 20, mol of at least one alkylene oxide per mole of alcohol. The preferred alkylene oxide is ethylene oxide. The alcohols preferably have 10 to 18 carbon atoms.

- Alkylphenol alkoxylates, in particular alkylphenol ethoxylates, which comprise C_6-C_{14}-alkyl chains and from 5 to 30 mol of alkylene oxide/mole.

- Alkylpolyglucosides which comprise C_8-C_{22}-alkyl, preferably C_{10}-C_{18}-alkyl, chains and as a rule from 1 to 20, preferably from 1.1 to 5, glucoside units.

- N-Alkylglucamides, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates and block copolymers of ethylene oxide, propylene oxide and/or butylene oxide.

Examples of suitable anionic surfactants are:

- Sulfates of (fatty) alcohols of 8 to 22, preferably 10 to 18, carbon atoms, in particular C_9C_{11}-alcohol sulfates, $C_{12}C_{14}$-alcohol sulfates, C_{12}-C_{18}-alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate.

- Sulfated alkoxylated C_8-C_{22}-alcohols (alkyl ether sulfates): compounds of this type are prepared, for example, by first alkoxylating a C_8-C_{22}-alcohol, preferably a C_{10}-C_{18}-alcohol, e.g. a fatty alcohol, and then sulfating the alkoxylation product. Ethylene oxide is preferably used for the alkoxylation.

- Linear C_8-C_{20}-alkylbenzenesulfonates (LAS), preferably linear C_9-C_{13}-alkylbenzenesulfonates and -alkyltoluenesulfonates.

- Alkanesulfonates, in particular C_8-C_{24}-alkanesulfonates, preferably C_{10}-C_{18}-alkanesulfonates.

- Soaps, such as the Na and K salts of C_8-C_{24}-carboxylic acids.

The anionic surfactants are preferably added in the form of salts. Suitable cations are, for example, alkali metal ions, such as sodium, potassium and lithium, and ammonium salts, such as hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium salts.

Examples of particularly suitable cationic surfactants are:

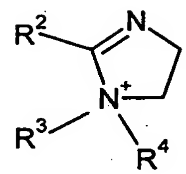
- C_7-C_{25}-alkylamines;

- N,N-dimethyl-N-(hydroxy-C_7-C_{25}-alkyl)ammonium salts;

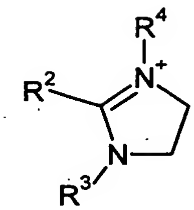
- mono- and di-(C_7-C_{25}-alkyl)dimethylammonium compounds quaternized with alkylating agents;

- ester quats, in particular quaternized esterified mono-, di- and trialkanolamines which have been esterified with C_8-C_{22}-carboxylic acids;

- imidazoline quats, in particular 1-alkylimidazolinium salts of the formulae III or IV



III



IV

where

R^2 is C_1-C_{25}-alkyl or C_2-C_{25}-alkenyl;
R^3 is C_1-C_4-alkyl or hydroxy-C_1-C_4-alkyl;
R^4 is C_1-C_4-alkyl, hydroxy-C_1-C_4-alkyl or a radical R^4-(CO)-X-$(CH_2)_p$- (X:-O- or -NH-; p: 2 or 3),

at least one radical R^2 being C_7-C_{22}-alkyl.

Of course, a plurality of different surfactants may also be used. A person skilled in the art makes a suitable choice from among the surface-active substances depending on the desired application. Proposed formulations are described in the relevant literature, for example the technical information from BASF AG, Technische Reinigungsmittel, January 1993 edition.

Nonionic surfactants are preferably used.

The formulation used particularly preferably comprises one or more water-soluble complexing agents as further components. The complexing agents have a synergistic effect together with the pickling inhibitor. It has been found that, when added to pickling acids, complexing agents accelerate the removal of metal. If, however, they are used in combination with the alkoxylated alkynols employed as pickling inhibitors in accordance with the invention, the inhibiting effect of the pickling inhibitor is not reduced by the complexing agent but on the contrary is even enhanced. In experiments, it was possible to improve the inhibiting effect by up to 60% by adding a complexing agent.

The complexing agent is a water-soluble, at least bidentate ligand which is capable of forming chelate complexes. The ligand comprises acidic groups, preferably COOH groups. As below, the complexing agent has at least two COOH groups. A bidentate to hexadentate ligand is preferred, and a bidentate to tetradentate ligand is particularly preferred. A person skilled in the art knows that the coordinating groups in a chelate-forming ligand are arranged in such a way that the ligand together with the metal can form one or more rings, in particular five-membered rings.

The ligand can moreover comprise other atoms or groups which are capable of forming coordinate bonds to metal ions. Examples of these are in particular OH groups and nitrogen-containing groups, such as primary, secondary and tertiary amino groups. Tertiary amino groups are preferred.

Complexing agents preferred for carrying out this invention comprise ligands which are derived from compounds which have primary amino groups and in which the H atoms on the amino group are substituted by $-CH_2-COOH$ groups. Examples comprise ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA) or methylglycinediacetic acid (MGDA). Ethylenediaminetetraacetic acid and methylglycinediacetic acid are preferably used for carrying out the present invention, and methylglycinediacetic acid is very particularly preferred. The complexing agent can be used in the form of acids or in the form of salts.

The complexing agents may also be polymeric complexing agents. Suitable polymeric complexing agents are in particular those which are derived from polymers which have primary and/or secondary amino groups and in which some or all of the H atoms on the amino groups have been substituted by $-CH_2-COOH$ groups. Preferred polymeric complexing agents are polyethyleneimines modified with $-CH_2-COOH$ groups. As a rule, at least 50%, preferably at least 60%, particularly preferably at least 75%, of the H atoms on the amino groups should be substituted. The preparation of such polymeric complexing agents is described in WO 2004/001099.

The person skilled in the art in the area of water-soluble complexing agents knows that the solubility of COOH-containing complexing agents in water may be dependent on the pH. The pH chosen for the respective intended use should therefore be selected as a reference point in each case. A complexing agent which has insufficient solubility for the intended use at a certain pH may have a sufficient solubility at another pH.

If present, the complexing agent is as a rule used in an amount of from 0.01 to 10% by weight. From 0.1 to 10% by weight are preferably used, particularly preferably from 0.1 to 5% by weight .

The weight ratio of complexing agent to pickling inhibitor is as a rule from 100:1 to 1:100, preferably from 50:1 to 1:50, particularly preferably from 5:1 to 1:10. Depending on the acid concentration, the following amounts have proven particularly appropriate for use at room temperature.

Amount of acid [% by weight]	Pickling inhibitor [% by weight]	Complexing agent [% by weight]
5	0.01 - 0.05	0.01-0.05
10	0.01 - 0.1	0.01-0.5
15	0.05 - 0.2	0.01-1
20	0.1 - 0.25	0.01-1

The pH of the composition is determined by a person skilled in the art according to the intended use. It can be established by the type and amount of the acid and, if appropriate, further components, depending on the intended use. Suitable buffer systems, e.g. phosphate buffer or citrate buffer, can also be used for stabilizing the pH. As a rule, the pH is from 0 to less than 7, preferably from 6.5 to 2, particularly preferably from 3 to 6.

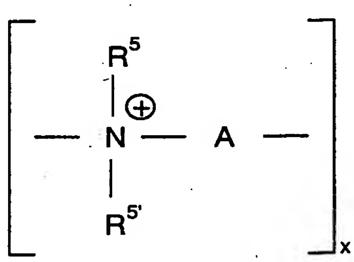
The formulation which comprises

(a) from 60 to 99.97% by weight of a mixture of water and at least one acid,
(b) from 0.01 to 2% by weight of at least one of said alkyne alkoxylates,
(c) from 0.01 to 20% by weight of at least one surface-active substance and
(d) from 0.01 to 10% by weight of at least one of said chelate-forming complexing agents

is particularly preferred for carrying out the novel process.

Very particularly preferably, the amounts are : (a) from 70 to 98.9% by weight, (b) from 0.1 to 2% by weight, (c) from 0.5 to 15% by weight, and (d) from 0.5 to 10% by weight.

In a further preferred embodiment of the invention, the pickling inhibitors used according to the invention are used together with water-soluble cationic, nitrogen-containing polymers (V) which comprise quaternized ammonium groups

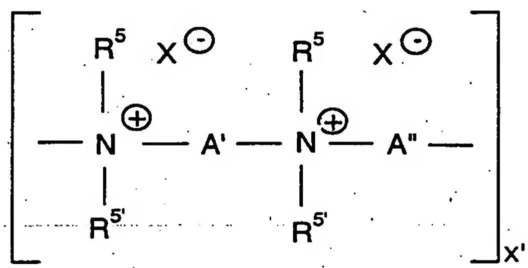


(V)

R^5 and $R^{5'}$ being identical or different and being saturated or unsaturated, substituted or unsubstituted aliphatic radical, saturated or unsaturated, substituted or unsubstituted alicyclic radical or substituted or unsubstituted araliphatic radical. The groups A linking the ammonium groups are hydrocarbon groups, in particular alkylene groups in which further functional groups and/or heteroatoms may also be incorporated. For example,

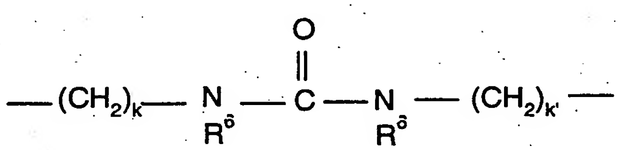
nonneighboring groups can be replaced by O atoms or N atoms. Suitable functional groups are in particular urea groups –NC-CO-NH-. X is chosen by a person skilled in the art according to the desired properties. Particularly suitable polymers usually have a molecular weight of 1000 – 100 000, preferably 1500 – 50 000, particularly preferably 2000 – 20 000 g/mol.

The cationic polymer V is preferably one which comprises two different linking groups A' and A".



As shown, the radicals A' and A" can preferably be arranged so that they are alternating, but they can also in principle occur in any desired sequence and number in the polymer.

The group A' is a group which comprises alkylene units and urea units:

 (A')

here, k and k', independently of one another, are each a natural number from 1 to 5, preferably 2 or 3. R^6 and $R^{6'}$, independently of one another, are H or a straight-chain or branched alkyl radical of 1 to 12 carbon atoms. R^6 and $R^{6'}$ are preferably selected from the group consisting of H, $-CH_3$ and $-C_2H_5$, and R^6 and $R^{6'}$ are particularly preferably H.

The group A" is a straight-chain or branched alkylene group of 2 – 20 carbon atoms. The group may be substituted by groups such as –OH or =O. Furthermore, non-neighboring, nonterminal carbon atoms may also be substituted by one or more identical or different heteroatoms, such as O, S and/or N. O-substituted radicals are preferred.

A" is preferably a radical of the formula

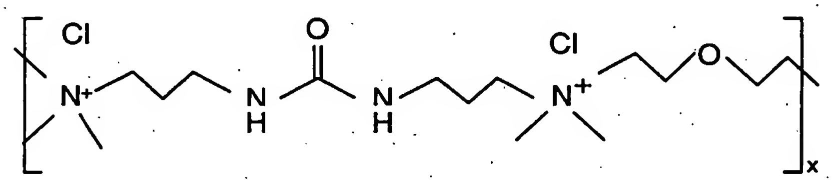
$$-CH_2CH_2-(OCH_2CH_2)_l- ,$$

where l is a natural number from 1 to 3. A" is particularly preferably

$-CH_2CH_2-O-CH_2-CH_2-$.

Such cationic polymers, their preparation and properties are known in principle, in particular as cosmetic hair compositions. For example, reference may be made to DE-A 25 21 960 or DE-A 2 924 230.

It is particularly preferably a polymer of the formula VI:



The cationic polymers are preferably used in the same amounts as the complexing agents. Of course, both complexing agents and cationic polymers may also be used together with the pickling inhibitor.

The formulation used may also comprise further components or assistants, depending on the intended use.

In order to improve the removal of greases in the degreasing by pickling, it may be advantageous to add small amounts of water-miscible organic solvents to the composition. The amount of optionally added organic solvents is, as a rule, from 0 to 10% by weight. Examples of suitable, water-miscible solvents comprise monoalcohols, such as methanol, ethanol or propanol, higher alcohols, such as ethylene glycol or polyetherpolyols, and ether alcohols, such as butyl glycol or methoxypropanol.

Examples of further assistants comprise, for example, antifoams, such as polypropoxylates or silicone ethers. The type and amount of additional components or assistants are determined by a person skilled in the art according to the intended use. The amount of optionally added further assistants is as a rule from 0 to 5% by weight.

In addition to the abovementioned components, formulations for phosphating comprise zinc ions, phosphate ions and, if appropriate, further components, such as fluoride in particular complex fluorides, accelerators, such as nitrite ions or further metal ions, such as manganese, copper, magnesium or nickel ions. Acidic formulations for phosphating are disclosed, for example, in WO 99/32687, DE-A 199 23 084 or DE-A 197 23 084.

In the novel process, the metallic surface is brought into contact with the aqueous formulation, for example by spraying, dipping or rolling on. After a dipping process, the workpiece can be allowed to drip to remove excess treatment solution; however, in the case of metal sheets, metal foils or the like, excess treatment solutions can, for example, also be squeezed out.

It is of course also possible to treat metallic surfaces in the interior of plants. Internal deposits in boilers, pipelines or the like can be removed by filling the plant with the formulation used according to the invention or flushing it therewith. The dissolution of the deposit can be accelerated by circulating the formulation in the plant by pumping.

The novel process can optionally also comprise one or more pretreatment steps. For example, the metallic surface can be cleaned prior to pickling with the formulation used according to the invention, for example to remove greases or oils. This is especially advisable in particular in the case of phosphating.

Furthermore, the process may optionally comprise aftertreatment steps. Examples of these are in particular washing steps in which the treated surface is washed with suitable cleaning liquids, in particular water, in order to remove, for example, residues of the formulation used according to the invention from the surface.

It is also possible to employ no-rinse processes in which the treatment solution is dried in immediately after application, without washing off, directly in a drying oven.

The treatment can be carried out batchwise or continuously. A continuous process is particularly suitable for treating strip metals. Here, the metal strip is passed through a tank or a spray apparatus and optionally through further pretreatment or aftertreatment stations.

Temperature and duration of the treatment are determined by a person skilled in the art according to the intended use. A higher temperature accelerates on the one hand the pickling attack on layers to be removed but, on the other hand, also the pickling attack on the metal itself. In general, the temperature of the treatment is from 20 to 80°C, without there being any intention thereby to limit the invention to this range. The duration of treatment may be from 1 second to several hours. Usually, the duration of treatment is shorter at higher temperatures than at lower temperatures.

In the pickling of steel strips, a temperature of from 60 to 80°C, for example 70°C, in combination with contact times of from 1 to 10 seconds has proven particularly useful. For steel strips, pickles containing sulfuric or hydrochloric acid are particularly suitable.

In the novel process, the pickling attack on the metal is inhibited substantially more

strongly than with the use of unalkoxylated pickling inhibitors. Complexing agents have a synergistic effect together with the alkoxylated pickling inhibitors and substantially reduce the pickling attack further.

In a further preferred embodiment of the invention, the acidic, aqueous composition can be used as a fountain solution for offsetting. The ethoxylated alkynols present in the formulation advantageously prevent undesired corrosion on printing press and printing plates. Suitable acids for this application are in particular phosphoric acid or organic acids, such as, for example, succinic acid, usually as components of a buffer system.

The conventional additives known to a person skilled in the art can be used as further components for this application. Examples comprise alcohols, such as glycerol, hydrophilic polymers, such as gum arabic or cellulose derivatives, surface-active substances and biocides.

The examples which follow illustrate the invention:

Abbreviations used:

PA:	Propargyl alcohol
BDA:	2-Butyne-1,4-diol
EO:	Ethylene oxide
PO:	Propylene oxide
PA – n EO:	Propargyl alcohol ethoxylated with on average n ethylene oxide units
PA – n PO:	Propargyl alcohol propoxylated with on average n propylene oxide units
BDA – n EO:	2-Butyne-1,4-diol ethoxylated with on average n ethylene oxide units
BDA – n PO:	2-Butyne-1,4-diol propoxylated with on average n propylene oxide units

Preparation of the pickling inhibitors:

The preparation of the alkoxylated used for the novel process was effected on the basis of the method disclosed in DE-A 22 41 155.

The preparation of an ethylene oxide adduct starting from propargyl alcohol is described below by way of example.

Ethoxylated propargyl alcohol (PA – 2 EO)

In a 6 l pressure-resistant reactor having an anchor stirrer, temperature control and nitrogen inlet, 1200 g of propargyl alcohol are reacted with 24 g of triphenylphosphine and with 2 equivalents of ethylene oxide or propylene oxide in the course of 12 hours under a nitrogen atmosphere at 55-65°C.

Formulations used:

The following solutions were used for the examples:

Cleaning agents

Solutions 1 to 3

In each case solutions of corrosion inhibitor (if present) and complexing agent (if present) in water were prepared. The amounts of corrosion inhibitor and complexing agent are shown in each case in tables 1 to 4. The pH was established in each case with an acid. The total amount was in each case 100 g.

Solution 1	brought to pH 3.5 with 15% strength HCl
Solution 2	brought to pH 1 with concentrated H_2SO_4
Solution 3	brought to pH 3.5 with concentrated H_3PO_4

Pickling degreasers

Solution 4	1 g	pickling inhibitor (according to table 5)
	3 g	nonionic surfactant: saturated C_{13}-oxo alcohol, ethoxylated, on average 8 EO units
	0.2 g	anionic surfactant: acidic phosphoric ester of a fatty alcohol alkoxylate
	50 g	conc. HCl. (37% HCl)
	45.8 g	water
	Water content:	77.3%
	Content of water + acid:	95.8%

Solution 4a	as for solution 4, additionally 0.2% by weight of methylglycinediacetic acid (0.2% by weight of water less)

Solution 5	1 g	pickling inhibitor (according to table 5)
	3 g	nonionic surfactant: saturated C_{13}-oxo alcohol, ethoxylated, on average 8 EO units
	3 g	3-nitrobenzenesulfonic acid
	0.5 g	alkylphenol ether sulfate, Na salt, 40% strength
	50 g	conc. HCl (37% HCl)
	42.5 g	water
	Water content:	74.3%
	Content of water + acid:	92.8%

Solution 6	2 g	pickling inhibitor (according to table 5)
	0.5 g	nonionic surfactant: oleylamine, ethoxylated, on average 12 EO units
	0.5 g	nonionic surfactant: saturated C_{13}-oxo alcohol, ethoxylated, on average 8 EO units
	25 g	conc. H_2SO_4 (96%)
	72 g	water
	Water content:	73 %
	Content of water + acid:	97%

Acidic rust remover

Solution 7	1 g	pickling inhibitor (according to table 5)
	12 g	nonionic surfactant: saturated $C_{13\text{-}15}$-oxo alcohol, ethoxylated, on average 8 EO units
	5 g	dodecylbenzenesulfonic acid
	40 g	conc. H_3PO_4 (85%)
	42 g	water
	Water content:	48%
	Content of water + acid:	82%

Solution 7a as for solution 7, additionally 0.2% by weight of methylglycinediacetic acid (0.2% by weight of water less)

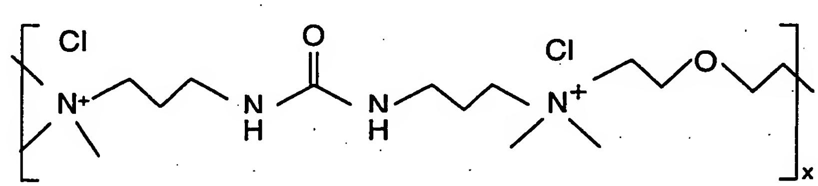
Acidic cleaning agents

Solution 8	5 g		pickling inhibitor (according to table 5)
	8 g		nonionic surfactant: saturated C_{13}-oxo alcohol, ethoxylated, on average 12 EO units
	50 g		conc. H_3PO_4 (85%)
	37 g		water
	Water content:		44.5%
	Content of water + acid:		87%

Polymeric complexing agents and cationic polymers as additives

In each case 0.5% strength solutions of corrosion inhibitor (if present) and 0.25% strength solution of complexing agent (if present) in water were prepared. The total amount was in each case 100 g.

Solution 9	0.5 g of pickling inhibitor, brought to pH 1 with concentrated H_2SO_4 and dissolved with 50 g/l Fe(II) sulfate.
Solution 10	As for solution 9, additionally 0.25% by weight of methylglycine-diacetic acid
Solution 11	As for solution 9, additionally 0.25% by weight of a polymeric complexing agent (polyethyleneimine, modified with acetic acid groups, Na salt)
Solution 12	As for solution 9, additionally 0.25% by weight of a cationic polymer of the formula



General experimental method:

1. Measurement principle:

Defined test sheets of St 1.0037, Al 99.9 or Zn 99.8 are each dipped into a constant test solution (see solutions 1-7) for 1 hour or 24 hours at room temperature, and the mass loss per unit area is determined gravimetrically by

means of differential weighing.

The preparation and cleaning of the metal sheets are effected according to ISO 8407 in a material-specific manner and is mentioned explicitly here for St 1.0037.

2. Preparation of the metal sheets:

Degreasing: In a plastic tank having two sheet-like electrodes (stainless steel or graphite) which are larger than the test sheet, a solution of the degreasing bath of the following composition is used:

20	g	of NaOH
22	g	of Na_2CO_3
16	g	of $Na_3PO_4 \cdot 12\,H_2O$
1	g	of ethylenediaminetetraacetic acid (EDTA)
0.5	g	of nonionic surfactant: alkylphenol, ethoxylated, on average
10		EO units in about 940 ml of demineralized water

NaOH, Na_2CO_3 and Na_3PO_4 are dissolved in succession in demineralized water with stirring. At the same time, EDTA and the surfactant are predissolved separately in demineralized water, this being effected in the case of the surfactant solution at a temperature of 50°C. The solutions of EDTA and surfactant are then added to the sodium hydroxide solution in a measuring cylinder and, after cooling, are made up to 1000 ml with demineralized water.

Rust removal: In a plastic tank having two sheet-like electrodes which are larger than the test sheet, a solution of the rust removal bath of the following composition is used: 100 g of diammonium citrate in 1000 ml of water with demineralized water.

A steel sheet measuring 50 mm x 20 mm x 1 mm is wiped with a paper cloth and dipped into the degreasing bath between the electrodes at 10 volt and is connected as the cathode. The voltage is adjusted so that the current is 1 A. After ten seconds, the steel sheet is removed and is washed with running water for five seconds.
The steel sheet is dipped into the rust removal bath between the electrodes at 10 V and is connected as the cathode. The voltage is adjusted so that the current is 1 A. After three minutes, the steel sheet is removed and is washed with running demineralized water for five seconds, blown off with air and used directly for the test.

3. Pickling tests

The metal sheet measuring 50 mm x 20 mm x 1 mm is electrolytically degreased and derusted.

The initial mass is determined by means of an analytical balance. The metal sheet is used directly after the weighing. The prepared metal sheet is placed obliquely in a 200 ml glass bottle containing test solution. The angle between steel sheet and base is 35°. The glass bottle is closed firmly and stored at room temperature. During the storage, the glass bottle is shaken once briefly every 6 hours.

The metal sheet is removed from the solution, washed with demineralized water, brushed off with steel wool, washed with demineralized water and blown dry with air. The mass is then determined.

The gravimetric pickling test is carried out as a ten-fold determination and the mean value is calculated.

Simultaneously with the test, a ten-fold determination without pickling inhibitor and with but-2-yne-1,4-diol or propargyl alcohol as pickling inhibitor is carried out.

4. Evaluation of the results

For each metal sheet, the difference between first and second weighing in mg/cm^2 is noted (Δm_{Sample}). In addition, the efficiency E of the active substance, whereby the mass loss Δm_{Sample} is expressed in relation to the mass loss in the corrosion test without inhibitor, Δm_0, can be specified. The following is applicable:

$$E = (\Delta m_0 - \Delta m_{Sample}) / \Delta m_0$$

Accordingly, a maximum inhibition efficiency may be 1 (no removal of metal, or 0 (in demineralized water), but may also be < 0 if the introduction of an additive leads to accelerated corrosion.

Examples:

Tests without complexing agent

Examples 1 to 8, comparative examples 1 to 3

Solution 1 was used for the experiments (HCl, pH 3.5). The metal removal per unit area at 30°C after 1 hour and 24 hours and the inhibition efficiency E were determined for sheets of steel 1.0037 according to the method described generally above. The pickling inhibitors shown in table 1 were used in the amounts shown. A complexing agent was not present in these experiments. The results are summarized in table 1.

Examples 9 and 10, comparative examples 4 and 5

Solution 2 was used for the experiments (H_2SO_4, pH 1). The metal removal per unit area at 30°C after 1 hour and 24 hours and the inhibition efficiency E were determined for sheets of steel 1.0037 according to the method described generally above. The pickling inhibitors shown in table 2 were used in the amounts shown. A complexing agent was not present in these experiments. The results are summarized in table 2.

Synergistic mixture with complexing agent

Examples 11 to 18, comparative examples 6 and 7

Solution 1 was used for the experiments (HCl, pH 3.5). The inhibition efficiency E was determined for sheets of steel 1.0037 according to the method described generally above at room temperature after 1 hour. The pickling inhibitors and complexing agents shown in table 3 were used in the amounts shown. The results are summarized in table 3.

Examples 19 to 30, comparative examples 8 to 10

Solution 3 was used for the experiments (HCl, pH 3.5). The inhibition efficiency E was determined for sheets of steel 1.0037 according to the method described generally above at room temperature after 1 hour. The pickling inhibitors and complexing agents shown in table 4 were used in the amounts shown. The results are summarized in table 4.

Examples 31 to 42, comparative examples 11 to 15

The solutions 4 to 8 were used for the experiments (see above). The inhibition efficiency E was determined for sheets of steel 1.0037 according to the method

described generally above at room temperature after 1 hour. The pickling inhibitors and complexing agents shown in table 5 were used in the amounts shown. The results are summarized in table 5.

Table 1: Test with solution 1 (HCl, pH 3.5)

			Metal removal at 30°C [mg]		Inhibition efficiency E [%] after 1 h
No.	Pickling inhibitor	Amount [% by wt.]	After 1 h	After 24 h	
Comparative example 1	-	-	60	> 80	0
Comparative example 2	BDA	5	10	42	83
Example 1	BDA - 2 EO	5	8	35	86
Example 2	BDA - 2 PO	5	7	33	88
Comparative example 3	PA	5	16	68	73
Example 4	PA - 2 PO	0.5	12	55	80
Example 5	PA - 2 PO	1	8	25	86
Example 6	PA - 2 PO	5	2	16	97
Example 7	PA - 7 EO	5	14	65	77
Example 8	PA - 2 EO	5	3	18	95

Table 2: Tests with solution 2 (H_2SO_4, pH 1)

			Metal removal at 30°C [mg]		Inhibition efficiency E [%] after 1 h
No.	Pickling inhibitor	Amount [% by wt.]	After 1 h	After 24 h	
Comparative example 4	-	-	1.2	> 5	0
Comparative example 5	BDA	2	0.4	1.5	67
Example 9	BDA - 2 EO	1	0.3	1.2	75
Example 10	BDA - 2 PO	1	0.2	0.9	83

Table 3: Tests with solution 1 (HCl, pH 3.5)

No.	Pickling inhibitor		Complexing agent		Inhibition efficiency E
	Type	Amount [% by wt.]	Type	Amount [% by wt.]	[%] after 1 h
Comparative example 6	-	-	Nitrilotriacetic acid	1	- 60
Example 11	PA - 2 PO	0.5	-	-	44
Example 12	PA - 2 PO	0.5	Nitrilotriacetic acid	1	70
Example 13	PA - 2 EO	0.5	-	-	8
Example 14	PA - 2 EO	0.5	Nitrilotriacetic acid	1	50
Comparative example 7	-	-	EDTA	1	-40
Example 15	PA - 2 PO	0.5	-	-	44
Example 16	PA - 2 PO	0.5	EDTA	1	70
Example 17	PA - 2 EO	0.5	-	-	8
Example 18	PA - 2 EO	0.5	EDTA	1	70

Table 4: Tests with solution 3 (H_3PO_4, pH 3.5)

No.	Pickling inhibitor		Complexing agent		Inhibition efficiency E [%] after 1 h
	Type	Amount [% by wt.]	Type	Amount [% by wt.]	
Comparative example 8	-	-	Methylglycinediacetic acid	1	-35
Example 19	PA - 2 PO	0.5	-	-	44
Example 20	PA - 2 PO	0.5	Methylglycinediacetic acid	1	71
Example 21	PA - 2 EO	0.5	-	-	8
Example 22	PA - 2 EO	0.5	Methylglycinediacetic acid	1	35
Comparative example 9	-	-	Nitrilotriacetic acid	1	-16
Example 23	PA - 2 PO	0.5	-	-	44
Example 24	PA - 2 PO	0.5	Nitrilotriacetic acid	1	71
Example 25	PA - 2 EO	0.5	-	-	8
Example 26	PA - 2 EO	0.5	Nitrilotriacetic acid	1	29
Comparative example 10	-	-	EDTA	1	-27
Example 27	PA - 2 PO	0.5	-	-	44
Example 28	PA - 2 PO	0.5	EDTA	1	48
Example 29	PA - 2 EO	0.5	-	-	8
Example 30	PA - 2 EO	0.5	EDTA	1	48

Table 5: Testing of different cleaning, pickling or deliming formulations

Example No.	Solution No.	Pickling inhibitor	Complexing agent		Metal removal at 30°C [mg]
			Type	Amount [by wt.]	
Comparative example 11	4	BDA			0.015
Example 31	4	PA - 2 PO	-	-	0.005
Example 32	4a	PA - 2 PO	Methylglycinediacetic acid	0.2	0.003
Example 33	4	PA - 2 EO	-	-	0.012
Comparative example 12	5	BDA	-	-	0.480
Example 34	5	PA - 2 PO	-	-	0.068
Example 35	5	PA - 2 EO	-	-	0.195
Comparative example 13	6	BDA	-	-	0.105
Example 36	6	PA - 2 PO	-	-	0.010
Example 37	6	PA - 2 EO	-	-	0.090
Comparative example 14	7	BDA	-	-	0.015
Example 38	7	PA - 2 PO	-	-	0.090
Example 39	7a	PA - 2 PO	Methylglycinediacetic acid	0.2	0.075
Example 40	7	PA - 2 EO			0.110
Comparative example 15	8	BDA	-	-	1.710
Example 41	8	PA - 2 PO	-	-	0.613
Example 42	8	PA - 2 EO	-	-	0.620

Table 6: Test with solution 9 (H_2SO_4, pH 1), comparison of different additives

	Pickling inhibitor PA-2-PO	Type of additive	Amount of additive [% by weight	Metal removal at 50°C Duration of action 15 min	Inhibition efficiency E [%]
Comparative example 16	0.5	-	-	0.03	96
Comparative example 17	-	Cationic polymer	0.5	0.045	80
Example 43	0.5	Cationic polymer	0.5	0.011	>99
Example 44	0.5	Polymeric complexing agent	0.25	0.010	>99

The examples show that the alkoxylated pickling inhibitors used according to the invention effect considerable better inhibition than propargyl alcohol or butynediol. Thus, not only was a substitute which is safer from the economical point of view provided, but even a substitute having a better action. This applies in particular to steel surfaces.

Moreover, they surprisingly cooperate in a synergistic manner with complexing agents. Whereas the complexing agent when used alone even accelerates the dissolution of the metal, the combination of complexing agent and pickling inhibitor results in even greater inhibition than with the pickling inhibitor alone.